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MEASUREMENT OF HO$_2$ AND OTHER TRACE GASES IN THE STRATOSPHERE

USING A HIGH RESOLUTION FAR-INFRARED SPECTROMETER AT 28 KM

GRANT NSG 5175

Semiannual Status Report No. 14

For the Period 1 January 1984 to 30 June 1984

Principal Investigators
Dr. Wesley A. Traub
Dr. Kelly V. Chance

September 1984

The Smithsonian Astrophysical Observatory
is a member of the
Harvard-Smithsonian Center for Astrophysics

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Prepared for
National Aeronautics and Space Administration
Greenbelt, Maryland 20771

Smithsonian Institution
Astrophysical Observatory
Cambridge, Massachusetts 02138

I. Personnel Working on this Grant During this Reporting Period

Dr. Wesley A. Traub (Principal Investigator)

Dr. Kelly V. Chance (Principal Investigator)

Dr. Stephen C. Wofsy (Co-Investigator)

II. Status Summary

During this reporting period we worked on data analysis from our 1983 BIC-I and II balloon flights, with emphasis on H_2O_2, OH, HCl, HF, O_3, O_2, and H_2O. Results were presented at a BIC data meeting, at a workshop on the stratosphere near Munich, West Germany, and in a paper submitted for publication (H_2O_2). Finally, we have begun design work on our major new effort, the building of a new far-infrared spectrometer and stratospheric telescope to replace the system destroyed in the BIC-II free-fall. A fuller discussion of each of these areas follows.

(1) H_2O_2. We completed our search for stratospheric H_2O_2 in our January 1983 flight spectra. From our analysis of the most sensitive clean spectral feature of hydrogen peroxide in the far-infrared, the $^RQ_5$ branch at 112.2 cm^{-1}, we have set a 2 sigma upper limit on its abundance as a function of altitude. In the altitude range where we were most sensitive for H_2O_2 detection, between 26 and 34 km, we find a 2 sigma upper limit which is comparable to or less than theoretically predicted winter abundances from the 2-D models of du Pont and of AER, at our latitude of observation. A copy of the paper describing this work (subsequently accepted by JGR Atmospheres) is included with

this report as Appendix A.

These measurements represent the most sensitive search for H_2O_2 yet made in the atmosphere. In the near future we intend to extend the analysis to our June 1983 flight data. Both models predict a winter minimum in H_2O_2, with a summer maximum that is sufficiently large to make definite concentration profile measurements a distinct possibility. Future measurements of this molecule will be greatly enhanced by the increased sensitivity and greater resolution (allowing the measurement of up to four ^RQ branches) of our new spectrometer.

(2) OH. We have begun to extract both vertical and temporal abundance profiles for OH from our June 1983 flight spectra. This is summarized briefly in the attached figure, which was prepared for the June 1984 meeting "Current Issues in our Understanding of the Stratosphere and the Future of the Ozone Layer", where Dr. Traub presented results for both OH and H_2O_2. As shown in the figure, there is a clear and dramatic drop in OH from day to night, as generally anticipated from photochemical theory but never before directly measured in the stratosphere. Note that the reduction of OH is not total in the nighttime scans. There are small remaining OH lines that we currently believe to be from mesospheric OH.

Vertical profiles from 3 of the 12 available OH lines are shown. The measured trend follows, in a very rough sense, two available model profiles (from M. Prather and A. J. Owens), but more analysis is required before we can make definitive

comparisons. Active work is continuing in this area.

(3) HCl and HF. HCl is our "prime molecule" for the BIC intercomparison. At the 2nd BIC data analysis meeting, in Paris at ONERA in May 1984, we presented our vertical profiles for HCl and HF. Although our results, as well as those of most others, were still preliminary, we were very encouraged by the amount of agreement among the majority of the profiles (including ours). An important result from this meeting was the discovery that one of our two HF lines was contaminated by a weak H_2O line, which explained a large systematic difference we had observed, and improved the general agreement between HF measurements. The HCl and HF work is expected to be essentially complete, including modelling of the interfering water line, in time for the last BIC data meeting, in December 1984.

(4) O_3, O_2, and H_2O. We are analyzing our spectra for these molecules with emphasis on using them as checks on the overall retrieval process, more than as investigations from which we expect fundamental results. Since the O_3 profile was the best determined profile from the BIC-II campaign, we have tried to improve the accuracy of our retrieval in several ways, to approach the overall ability of various investigators for measuring ozone. One improvement was to fully recognize the dominant role of the far wings of H_2O lines in low-altitude spectra. This has been theoretically predicted by A. Clough at AFGL, and appears to be verified in our spectra. The strength of these wings exceeds that of many molecular line cores (including

O_3 and O_2) for our lowest elevation spectra, especially near the long wavelength (100 cm^{-1}) end of the spectra. Another place for improvement has been in the knowledge of line center positions and pressure broadening coefficients. We have obtained from B. Carli et al. a set of newly-measured positions for O_3, which noticeably improves our least-squares fitting procedure. We have also begun to work closely with R. Gamache of the University of Lowell, who has provided us with newly-calculated O_3 and H_2O broadening parameters; these often differ substantially from the values in the AFGL line listing, and we have been able to retrieve very good O_3 profiles with the new parameters. The O_2 work is important in that it directly checks our retrieval process, since O_2 has a known, constant mixing ratio. These efforts are currently quite active and will continue at least until the December 1984 BIC data meeting.

(5) Rebuilding. The instrument rebuilding effort began in the middle of this reporting period. We have made good progress, particularly in the area of electronics. The mechanical design was somewhat slower, but with the hiring of a senior mechanical engineer in June 1984 we began to move rapidly. As of the end of this reporting period, we have completed most of the design of the stabilized platform, and part of the design of the telescope. A preliminary optical layout was completed, incorporating our new higher resolution (0.004 cm^{-1} versus 0.032 cm^{-1}, unapodized). The 8-fold increase in optical path difference was accomplished with only a modest increase in

spectrometer weight. Since the end of the reporting period, a
final optical layout has been adopted, with the detailed design
proceeding rapidly. As expected, the rebuilding work is
consuming a large fraction of our time, at the expense of data
analysis. Our current schedule projects the completion of
assembly and start of laboratory testing in July 1985.

III. Publications and Presentations

(1) "An Upper Limit for Stratospheric Hydrogen Peroxide", Chance and Traub, to appear in JGR Atmospheres.

(2) Seminars on our stratospheric measurement program, by Traub, at the Division of Engineering and Applied Physics, Harvard University, in February, and at the Air Force Geophysical Laboratory, in March.

(3) "HCl and HF Intercomparison Studies", by Chance and Traub under CMA sponsorship (included here for completeness, as Appendix B).

(4) Presentation of BIC-I and BIC-II preliminary results, by Traub and Chance, at ONERA, in May.

(5) Presentation of OH and H_2O_2 preliminary results, by Traub, at Munich workshop, in June.
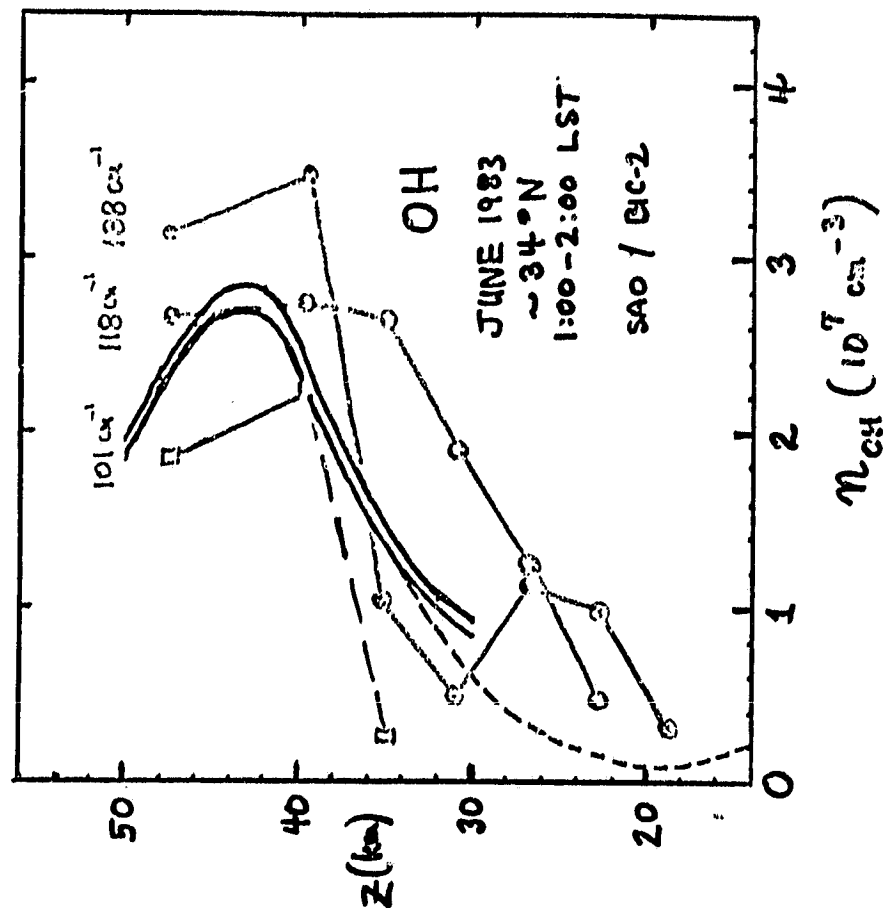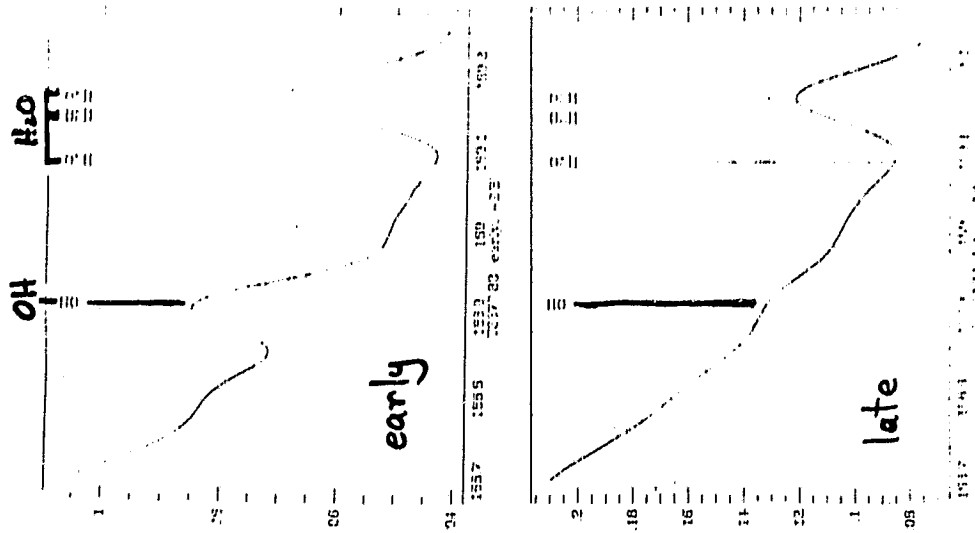
(Left) Thermal emission spectrum showing OH rotational line complex near 189.1 cm^{-1} and H_2O rotational line near 188.9 cm^{-1}. The "early" spectrum taken in the early afternoon at a balloon altitude of 37.6 km shows a clear OH feature having a measured peak intensity of about 0.02 of a 277 K blackbody over a resolution interval of 0.064 cm^{-1}. The "late" spectrum taken several hours after sunset at a lower altitude of 34.7 km shows only a very weak feature at the OH position, indicating a nearly complete absence of OH. The effective sampling altitudes are 31.0 and 28.1 km, respectively.

(Right) Preliminary vertical profile of OH for 3 spectral lines at 101, 118, and 188 cm^{-1}. The scatter in number density at any given altitude results from uncertainties in the retrieval caused by a combination of spectral noise and as-yet incompletely modeled spectral background. The smooth solid curves are from independent model calculations by M. Prather and A. Owens. These profiles are extremely preliminary, and should not be considered definitive.

Appendix A

An Upper Limit for Stratospheric Hydrogen Peroxide

AN UPPER LIMIT FOR STRATOSPHERIC HYDROGEN PEROXIDE

K. V. Chance

and

W. A. Traub

Harvard-Smithsonian Center for Astrophysics
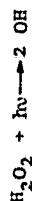
To appear in

ABSTRACT

2

We present measurements of an altitude-dependent upper limit for stratospheric hydrogen peroxide that is substantially lower than previously determined limits. The data were obtained with a remote-sensing far-infrared spectrometer during a balloon flight on 23 January 1983. Our 2 sigma upper limit is 0.05 ppbv near 26.5 km, and is larger above and below that altitude. This new upper limit is compared with two currently available modelling calculations for H_2O_2: in the neighborhood of 32 km, it is slightly lower than, but comparable to these theoretical profiles. The implications for measurement of H_2O_2 at different latitudes and seasons are briefly discussed.

INTRODUCTION

Hydrogen peroxide, H_2O_2, is postulated to be important in stratospheric chemistry as a reservoir and sink for odd hydrogen species and for its ability to interconvert them, chiefly through the reactions

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad (1)$$
$$H_2O_2 + h\nu \longrightarrow 2 \ OH \qquad (2)$$
$$H_2O_2 + OH \longrightarrow H_2O + HO_2 \ . \qquad (3)$$
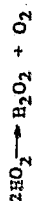
We are aware of two previous attempts to measure stratospheric hydrogen peroxide: first, Waters et al. [1981] have published a tentative measurement of 1.1 ± 0.5 ppbv between ~27 and ~35 km from microwave limb sounding data obtained on a balloon flight on 20 February 1981; second, there is an upper limit of $1-1.5 \times 10^{14}$ cm^{-2} above 30 km (which is equivalent to a mean mixing ratio of 0.4-0.6 ppbv), obtained from a ground-based millimeter-wave study in May-June 1983 (R. L. deZafra, J. W. Barrett, A. Parrish and P. R. Solomon, private communication, 1983). The present study yields an altitude dependent upper limit curve between 21.5 and 38.0 km for 23 January 1983 that is substantially below these previous values at all but the highest altitudes.

OBSERVATIONS AND CALCULATIONS

A. Balloon Flight and Instrumentation

The data used here are from balloon flight No. 1316-P, launched from the National Scientific Balloon Facility in Palestine, Texas (32° N) on 23 January 1983. Data were obtained between 2:00 and 3:00 pm CST at a float pressure of 5.50 ± 0.07 mbar, measured by a capacitance manometer provided by NSBF. From the pressure we determine an altitude of 35.1 ± 0.1 km, using the U. S. Standard Atmospheres January, 30° North atmosphere [U. S. Standard Atmospheres Supplements, 1966]. The spectra were taken in a limb-scanning mode, by measuring the thermal emission of the stratosphere, over a series of elevation angles between +30° and -3.9°. The elevation angles used in this paper and the tangent height at each angle are given in Table I. Eight interferograms, requiring 47.5 seconds each, were taken at each elevation, although as few as four are usable at some elevations because of problems with the recorded data. Spectra of an on-board blackbody reference source were also taken.

The measurements were made with a double-beam Fourier transform spectrometer [Traub et al., 1982] operating over the range 70 - 250 cm^{-1} at 0.064 cm^{-1} apodized resolution. For this flight Ge:Ga photoconductor detectors at 4 K were used.

The thermal radiation was collected and focussed onto the spectrometer's entrance aperture by a telescope with an 0.3° field of view, giving about 2 km vertical resolution at the tangent point for down-looking angles. The telescope elevation

was controlled by a stabilized pointing system capable of pointing in absolute elevation to $\pm 0.02°$, while rejecting gondola tilt and sway. The telescope and stabilized platform, which had their first field test on this flight, will be described in a separate publication.

The telescope, stabilized platform and spectrometer were mounted on a gondola supplied by the Jet Propulsion Laboratory, which gave azimuth control to $\pm 1°$. All spectra were taken with the telescope pointing at a true heading of 357 (± 3)°.

B. H_2O_2 Molecular Parameters

Hydrogen peroxide is a double barrier internal rotator with well determined mechanics [Hunt et al., 1965; Helminger et al., 1981]. The most prominent features in the far-infrared spectrum of H_2O_2 are narrow Q branches arising from a concurrent change in the torsional and rotational state of the molecule. The positions, shapes and widths, and strengths of the Q branches which are the most suitable for determination of stratospheric H_2O_2 were determined from various sources of data. Examination of the far-infrared spectrum of Hunt et al. [1965] showed a number of strong Q branches within the wavelength region of our spectrometer which were sufficiently sharp (at or near their spectral resolution of 0.4 cm^{-1}) to be attractive candidates for stratospheric work.

In order to more precisely define the peak positions and shapes of the Q branches, we measured laboratory spectra of H_2O_2 with the same instrument which we later used on the balloon

flight. Peak Q branch positions were obtained to an accuracy of ± 0.01 cm^{-1} by calibrating the spectra using residual H_2O lines in the spectrum [Kauppinen et al., 1978]. Comparison of our laboratory spectra of H_2O_2 and flight spectra showed that four Q branches, the $^RQ_4$ at 94.00 cm^{-1}, $^RQ_5$ at 112.20 cm^{-1}, $^RQ_6$ at 130.32 cm^{-1} and $^RQ_7$ at 148.36 cm^{-1}, were the best candidates for measurement of stratospheric H_2O_2. Fig. 1 shows a comparison between these Q branches in a sum of 10 laboratory spectra and a sum of 6 stratospheric spectra (-2.8°, tangent height = 27.4 km).

Of these four Q branches, the $^RQ_5$ is in the cleanest position in the stratospheric spectrum, and is the one used in the present determinations. The other three Q branches should be useful for atmospheric work with higher resolution instruments. The $^RQ_5$ branch is sufficiently narrow that it appears as a sharp line at our apodized resolution of 0.064 cm^{-1}. This is confirmed by calculations of Bowman, Helminger and De Lucia (W. C. Bowman, private communication, 1980), who predict for the $^RQ_5$ branch that all lines from J=6 to J=20 lie in an interval of width 0.039 cm^{-1}. These lines include over 90% of the population contributing to this Q branch at stratospheric temperatures. This narrowness is due to a coincidence, wherein the effect of a slight difference in the upper and lower torsional state rotational constants on line position is almost offset by the effect of centrifugal distortion. (The ^PQ branches, on the other hand, are further broadened by this effect.) The temperature

shift of the $^RQ_5$ branch position in going from laboratory to stratospheric temperature (i e., about 300 K to 230 K) is calculated to be approximately -0.01 cm^{-1}, by assuming an average position shift with J inside the Q branch envelope and calculating the wavenumber shift of J(max). This was also confirmed in calculations by Bowman (private communication, 1980).

Our laboratory spectra were not sufficiently quantitative to use as a source of H_2O_2 Q branch strengths for determination of stratospheric H_2O_2. To obtain strengths, we use the effective dipole moment between the n=0, τ=1,2 and n=0, τ=3,4 torsional states, μ_{01} = 1.58 ± 0.01 debye, taken from the measurements of Cohen and Pickett [1981], and calculate the appropriate statistical sums:

$$S(^RQ_K,T) = \frac{8\pi^3\mu_{01}^2\sigma(e^{\sigma/kT}-1)}{3hcQ_{rot}Q_{tors}}\sum_{J\geq K+1}\frac{(2J+1)(J+K+1)(J-K+1)(J-K)}{J(J+1)}\exp\left[\frac{-E'(J,K,torsion)}{kT}\right] \quad (4)$$

where the $S(^RQ_K,T)$ are the Q branch strengths in cm^{-1}/(molecule cm^{-2}), σ is the position of the Q branch in cm^{-1}, μ_{01} is in esu-cm and k is in cm^{-1}deg^{-1}. Q_{rot} and Q_{tors} are the rotational and torsional partition functions. The measured positions at room temperature and the calculated strengths at several temperatures of the $^RQ_4$, $^RQ_5$, $^RQ_6$ and $^RQ_7$ branches are given in Table II.

The strengths for individual lines calculated in this way are intrinsically quite accurate, since they are based directly on dipole moment measurements, and since the state-dependent effects of centifugal distortion and other vibrational-rotational interaction on the strengths are no more than a few percent for moderate rotational level transitions in light molecules. The major uncertainties in the Q branch strengths, which are sums of individual line strengths, are: (1) the possibility of interference by unassigned P and R branch lines (which would increase the effective strengths), and (2) the possibility that lines from J<6 and J>20, which account for less than 10% of the H_2O_2 population at stratospheric temperature, would not contribute to an observed spectral feature (which would decrease the effective strengths). Thus, an estimate of 10% for the total uncertainties of the Q branch strengths is quite realistic, and is assumed in our analysis.

C. Analysis of Spectra

The flight spectra are normalized in intensity by a 2-step procedure: first we subtract from all spectra a smoothed high elevation (+30°) spectrum, with its emission lines removed, to eliminate the residual unbalanced continuum in our 2-beam interferometer; second, we divide by a similarly processed 268 K blackbody reference spectrum, recorded during the flight. The spectra are then smoothed with a von Hann sliding 3-point weighting function (0.25, 0.50, 0.25) [Hamming, 1977] and, for

to obtain the best possible signal-to-noise ratio, so that in the subsequent analysis we are dealing with only one spectrum for each of the 6 elevation angles. A careful examination of spectra showed no features that are both consistent with the R_{Q_5} branch of H_2O_2 and also present in all spectra. The structure in the spectra in the interval 112.19 ± 0.03 cm^{-1} is not reproducible from spectrum to spectrum and is taken to be noise (the width of this interval is 4 times the 1σ uncertainty of the temperature shifted Q branch position). To determine the upper limit curve, integrated noise equivalent widths in the region of the R_{Q_5} branch were determined in two ways.

First, the peak-to-peak area of the largest structure with an extremum in the 112.19 ± 0.03 cm^{-1} region for each spectrum was integrated by computer between limits determined by a straight line drawn to isolate the extremum, as shown in Fig. 2(b) for the $+1.0°$ spectrum. The principal limitation of this technique is that the derived equivalent width is quite sensitive to the choice of baseline, i.e. the straight line between extrema in Fig. 2(b). Furthermore, this technique does not allow for local baseline curvature which may be present. For this reason we also employ the following, second, method.

To insure that there is no fortuitous cancellation of noise and spectrum at any particular elevation angle, two short sections of the apodized spectra outside of the bandpass of the detector and filter response were analyzed to give a reference noise level for the spectra. The rms fluctuations within these

presentation, are interpolated to a finer grid spacing (0.0032 cm^{-1}) by convolution with the theoretical apparatus function sin $\pi x/\pi x$, where x is in units of 0.03214 cm^{-1}. The overall intensity normalization can be accomplished in 2 ways, both leading to essentially equivalent results. First, we can directly use the on-board calibration scans of a blackbody whose temperature is monitored with 3 independent thermilinear elements. Second, we can use the spectrally localized blackbody which is generated in all but our highest elevation spectra by the saturated group of H_2O lines near 202 cm^{-1}. An advantage of this latter method, which is the one used in this paper, is that the narrow-band spectral flux from the saturated H_2O is given simply by the local stratospheric temperature, which we take to be the local temperature in our model atmosphere (see below), thereby tending to reduce any errors which might otherwise arise from imperfect knowledge of the stratospheric temperature profile. This normalizing factor, which is the same for all spectra to within ±3%, also tends to compensate for short-term variations in system sensitivity and change in sensitivity due to detector loading.

The uncertainty of the blackbody reference source spectral radiance at 202 cm^{-1} is 2.5%, from the combined effects of temperature measurement and emissivity uncertainties. Additional uncertainty from the intensity calibration is <5%.

The 112 cm^{-1} region of each spectrum used in the determination of the upper limit curve is shown in Fig. 2(a). The spectra from the two independent detectors are added together

regions, from 39-45 and 254-257 cm⁻¹, were measured over 1 cm⁻¹ intervals. Since the rms values from both regions and all elevation angles were comparable, an average value was calculated; finally, this average was multiplied by 1.56 to match the effect of spectral background subtraction and rescaling which was described above. The resultant average value of rms noise, 0.0022 of the spectral flux of a 268 K blackbody, was multiplied by 0.064 cm⁻¹, which is the width of the corresponding apodized spectral element. The result, which may be considered a globally averaged noise limit, is a noise equivalent width of 1.4×10^{-4} cm⁻¹. This corresponds to the area of the shaded box in Fig. 2(b).

The noise areas from both methods were corrected for the continuum level present in our spectra and for radiance at 112.2 cm⁻¹ by a multiplicative factor $F(\theta)$,

$$F(\theta) = [B(\sigma_o,T_e(\theta))/B(\sigma_o,T_{ref})-C(\theta)]^{-1} , \qquad (5)$$

where $C(\theta$ is the measured continuum spectral flux in the neighborhood of the R_{Q_5} position at limb-scan angle θ. $B(\sigma_o,T_e(\theta))$ is the blackbody spectral flux at 112.2 cm⁻¹ and the effective temperature of the airmass sampled by the ray at angle θ, and $B(\sigma_o,T_{ref})$ is the spectral flux at 112.2 cm⁻¹ of the reference blackbody. This correction is exact for an isothermal atmosphere or if the source of the continuum flux has the same altitude distribution as H_2O_2. It is a very good approximation

for the small temperature range sampled by the weighting function for each limb scan angle.

Both sets of corrected noise areas were then used to derive H_2O_2 upper limits, by the following procedure: (1) The noise areas are considered to be 1σ limits. (2) An additional 12% uncertainty is added, in quadrature, to the noise equivalent widths for the uncertainties in molecular strengths and widths, spectral calibration, telescope pointing ($\pm0.02° = 3\%$) and balloon altitude(±0.1 km = 1.5%). These results are multiplied by 2 to give a set of 2σ noise equivalent widths, including uncertainties, which are 2.01 times the original noise equivalent widths. (3) The sets of noise equivalent widths are divided by the R_{Q_5} strengths (Table II) appropriate to the effective temperature of each limb scan angle, to obtain upper limits on the H_2O_2 column density. (4) To obtain rigorous upper limits for mixing ratios we do not subtract contributions from higher layers in an onion-peeling fashion, but consider the upper limits on H_2O_2 column densities to apply to 1 scale height above the tangent height for each individual limb-scan angle. A set of atmospheric ray-tracing calculations was performed to determine the total column density of air in one density scale height. taken to be 6.4 km above the tangent height for each limb-scan angle, along the limb-scan line of sight. The effective heights (one-half airmass) for the line-of-sight geometries were also determined. The January, 30° North atmosphere [U. S. Standard Atmospheres Supplements, 1966] was used for these calculations. (5) The final upper limit mixing ratio values are obtained by

dividing the H_2O_2 column limits by the appropriate column densities. These are 2σ upper limits applicable to the effective heights for the respective limb-scan angles. They are appropriate for a latitude of about 34° North, as seen from the latitude of the balloon platform (32° North) with the telescope pointing northward.

The two sets of noise equivalent widths derived in (2) above, and the effective heights and temperatures are included in Table I. In practice, the limits from the second method of analysis, the overall noise limit, were larger in every case than the limits from the local measurements of noise areas. The larger limits are plotted in Fig. 3.

DISCUSSION

The H_2O_2 upper limit points shown in Fig. 3 are derived from the globally averaged noise limit, which in all cases is larger than the local measurements at the R_{Q_5} position for each summed spectrum. These points are connected with straight lines for ease in visual interpretation of the results. The overall shape of the resultant figure does not imply anything about the true shape of the stratospheric H_2O_2 profile, but is a measure of the relative sensitivity of our technique at different altitudes.

Recent two-dimensional calculations from the du Pont modelling program (A. J. Owens, private communication, 1983) and the Atmospheric and Environmental Research modelling program [Ko et al., 1984] are plotted in Fig. 3 for comparison with our

limit. Both calculations use the JPL 82-57 chemical rate set [JPL, 1982]. From the figure we see that our 2σ upper limit for H_2O_2 is very close to the du Pont model values for altitudes near 31 km. Our upper limit is slightly less than the AER model at altitudes from about 26 to 32 km. Uncertainties affecting the comparison of the measured upper limit and the model calculations include uncertainties in the rates for the major production and loss reactions listed earlier [JPL, 1982; JPL, 1983], uncertainties in the diurnally averaged concentrations of the reactants HO_2 and OH, and the possible effect of our measuring latitude, which is slightly farther North (34°) than the latitude in the calculations (30°). Both models predict a factor 3 to 4 increase in the summer concentration profile of H_2O_2 between 26 and 30 km. We have stratospheric limb-scan spectra from the BIC-II campaign in June 1983, currently in the process of data reduction, that should provide a much more conclusive test of the modelling of stratospheric hydrogen peroxide.

Our upper limit curve lies substantially below the Waters et al. [1981] tentative measurement of 1.1 ± 0.5 ppbv, even though the results are from the same latitude and are both wintertime measurements. For comparison with our results, we convert the previously mentioned upper limit of deZafra et al. (private communication, 1983) to an average mixing ratio: their limit of $1-1.5 \times 10^{14}$ cm^{-2} above 30 km becomes a mixing ratio of 0.4-0.6 ppbv above 30 km. This is to be compared with our limit of 0.1 ppbv from the -2.2° spectra, valid for 1 scale height

above 36.4 km. Both previously determined results are well above both sets of model predictions, even for summertime H_2O_2. The results of Waters et al. and of deZafra et al. are included in Fig. 3.

Upper limits or measurements of a single species are of course of limited use as tests of atmospheric chemical models because of the close coupling of the various chemical reactions, particularly among species involved in the same catalytic cycle, such as the HO_x species. The flight upon which the current H_2O_2 limit is based yielded good quality spectra of OH, H_2O, O_3, HCl and HF as well as the present H_2O_2 results. In the near future we should have a complete set of simultaneous altitude profiles of these other species.

ACKNOWLEDGEMENTS

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Figure Captions

Fig. 1. A comparison between stratospheric (top) and laboratory (bottom) emission spectra in the regions of the strongest R_Q branches of the rotational-torsional spectrum of H_2O_2 in our spectral region. The same spectrometer was used to measure both sets of spectra. The stratospheric spectrum (-2.8° elevation) is normalized to the 268 K blackbody reference. The laboratory spectrum is from approximately 2 torr H_2O_2 in a 61 cm cell at room temperature. The vertical scale for each laboratory spectral interval is normalized to the spectral radiance of a blackbody at the same temperature.

Fig. 2. (a) 112 cm^{-1} regions of stratospheric spectra, with the H_2O_2 line position (112.19 cm^{-1}) at stratospheric temperature indicated. All except the +1.0° spectrum are vertically displaced by arbitrary amounts to avoid overlap. (b) Detail from +1.0° spectrum showing area of extremum. The cross-hatched area beneath the curve is taken as the 1σ noise equivalent width for H_2O_2 as derived from the local spectrum at this elevation angle; this area leads to the noise measure NEQ(1) as described in the text. The shaded box indicates the 1σ noise level as measured in featureless regions of the spectrum, and leads to the noise measure NEQ(2). Since, for this elevation, the latter measure dominates, it is used to calculate the H_2O_2 upper limit shown in Table I.

Fig. 3. H_2O_2 measurements and 2-D model calculations. Short arrows are used to indicate upper limits for both the points presented in this paper and the box showing the dezafra et al. measurements. Our balloon altitude is indicated for reference.

Table I

Analysis of Limb-scan Data for Hydrogen Peroxide

Elevation angle	z_{tan} (km)	z_{eff} (km)	T_{eff} (K)	NEQ(1)[a] (10^{-4} cm^{-1})	NEQ(2)[a] (10^{-4} cm^{-1})	H_2O_2 lim.(ppbv)
+1.0°	35.1	38.0	245	0.4	3.3	0.52
-1.6°	32.6	33.5	237	-3.2	3.7	0.14
-2.2°	30.4	31.6	233	0.5	3.8	0.10
-2.8°	27.4	28.9	227	-3.0	4.5	0.07
-3.2°	25.1	26.5	222	0.7	5.0	0.05
-3.9°	20.1	21.5	212	11.4	15.8	0.08

[a] NEQ(1) and NEQ(2) are the 2σ noise equivalent widths from the individual limb scans at the position of $^RQ_5$, and from the reference noise level outside the instrument response region, respectively. They can be considered to be locally- and globally-determined measures of spectral fluctuations. In cases where NEQ(1) is negative, the sign would be dropped when calculating an H_2O_2 upper limit, but the limits from NEQ(2) are larger for all of the current data set.

Table II

Q Branch Positions and Strengths

Q Branch	Position (cm^{-1})	Strength(E-19 cm^{-1}/(molecule cm^{-2}))			
		(300K)	(250K)	(225K)	(200K)
$^RQ_4$	94.00	3.25	3.66	3.83	3.94
$^RQ_5$	112.20	2.69	2.74	2.68	2.53
$^RQ_6$	130.32	1.92	1.73	1.56	1.34
$^RQ_7$	148.36	1.19	0.932	0.767	0.585
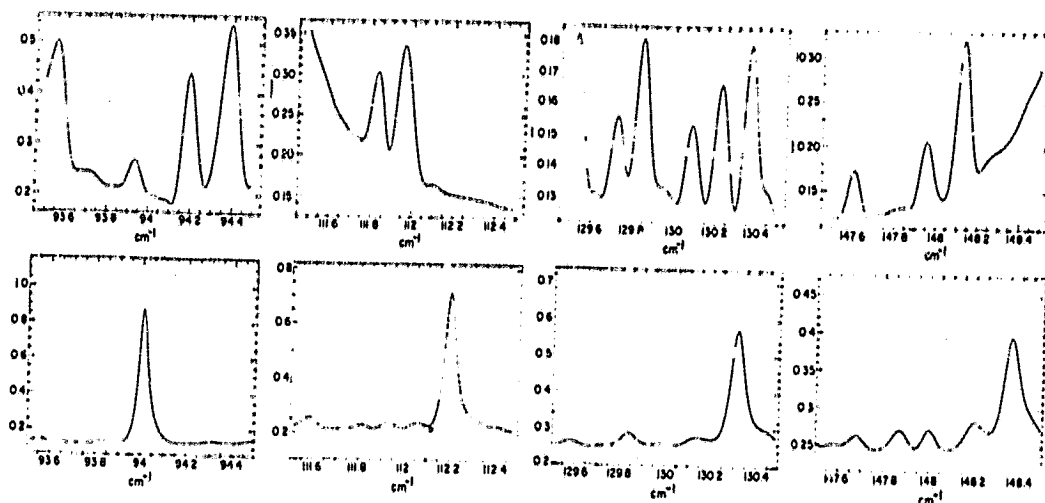
Fig. 1
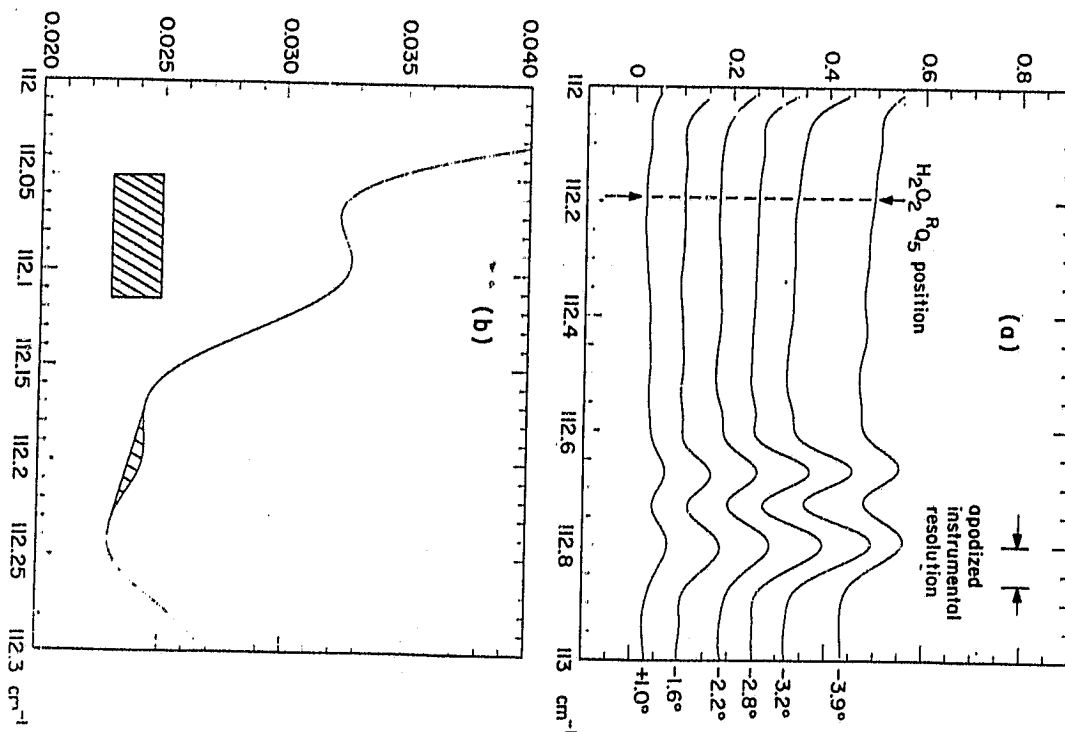
Fig. 2
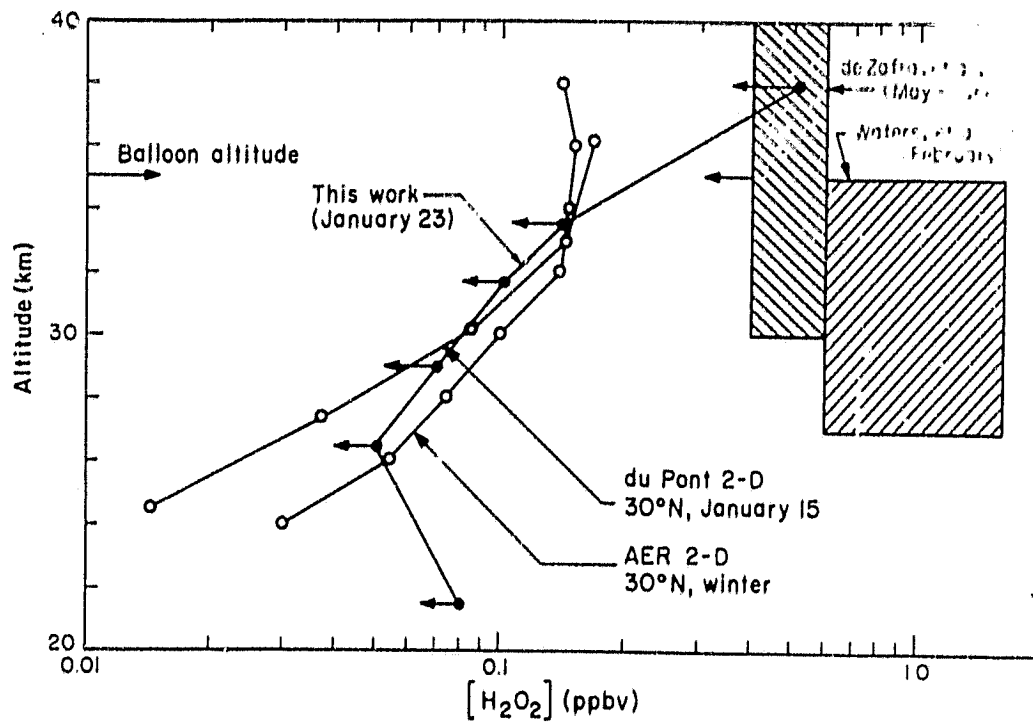
Fig. 3

4. HCl and HF Intercomparison Studies

As a part of our CMA-sponsored research, we have undertaken an intercomparison study of HCl and HF stratospheric measurements, including a literature survey of the determination of line parameters and of stratospheric measurements, and a mail survey of the investigators who have reported stratospheric measurements in the literature. The mail survey is now complete, with 10 of the 12 investigating groups responding, either by mail, by telephone or in person.

(A) Line parameters

The available line parameters have been partially discussed in our final report for contract FC 81-375. Also, it is worth noting the extensive effort by the HALOE group (Rinsland et al., 1982) in surveying the line parameters of these two molecules. Apart from the rather special requirements of HALOE, the greatest need at present is for more accurate strengths for the fundamental bands of both molecules and for more accurate pressure broadening coefficients for the rotational lines of both molecules. Fortunately, both of these needs are being addressed by research either in progress or planned for the immediate future. Line positions for both molecules are known to sufficient accuracy to satisfy all present atmospheric investigations.

HF Strengths for the vibrational fundamental can be determined, as in our final report for contract FC 81-375, to 8%

(1 sigma) accuracy from data presently in the literature. These values differ from the present AFGL catalog strengths by an average of 5%, for the R_0 to R_4 lines. The AFGL numbers come from the work of Ogilvie et al. (1980), who use experimental dipole moment matrix elements, including the value for the fundamental from Lovell and Herget (1962) to determine a power series expansion for the dipole moment function.

Data for the pressure broadening of the fundamental band of HF is very limited. Smith (1958) determined broadening efficiency ratios of foreign gases (including N_2 and O_2) to pure HF for the R_0 to R_4 lines. His study includes temperature dependence of the efficiency ratios for N_2/HF (measurements at 298 K and 373 K). These results must be used in conjunction with self-broadening coefficients of HF to obtain the appropriate pressure broadening coefficients. For self-broadening coefficients, see Beigang et al. (1979) and the review by Hough (1977). The AFGL numbers are probably adequate for determinations of HF above 25 km by solar absorption (i.e., their use probably causes no more than 10% error at 25 km), but the way they were actually determined is unclear. A careful, direct study of both self and foreign gas broadening coefficients is long overdue.

Strengths for the rotational lines of HF can be determined directly from the dipole moment to an accuracy of substantially better than 1%, even without making Herman-Wallis corrections. This has been shown in our CMA Quarterly Progress Report No. 2 to contract FC81-375, and in Tipping (1976).

Pressure broadening coefficients for the rotational lines of HF need to be determined, particularly since the stratospheric lines tend to be quite saturated. Determinations presently available include the N_2-broadened R_0 through R_4 lines, by Bachet (1972), which does not include experimental uncertainties, and a measurement of the N_2-broadened R_0 line by the IROE group. We have found no measurements of HF rotational line broadening by O_2 in the literature.

HCl   Strengths for the HCl fundamental have been determined by Toth et al. (1970), Babrov et al. (1959), Varanasi et al. (1972), Benedict et al. (1956) and Lin et al. (1978). Lin et al. claim to have suffered some loss of HCl on the cell walls. The other investigations all have errors, either stated or deduced from the papers, around 5%. Indeed, the strengths of the P_3 through R_5 lines from these investigations, for both isotopic species, have an rms deviation of 5% or less. The AFGL strengths, as for HF, come from Ogilvie et al. (1980). They use they rotationless dipole moment matrix element for the fundamental band from Smith (1973), who determines it as a best average of the infrared values and that obtained from the molecular beam work of Kaiser (1970). The present AFGL strengths should be good to 5% (1 sigma).

Pressure broadening coefficients of the HCl fundamental have been studied by a number of groups. Until recently though, the results reported in the literature have included very little temperature dependence and O_2 broadening information. Results

until recently are summarized in the HALOE document, to which
should be added Petrov and Podkladenko (1972) and Petrov (1975),
two Soviet studies that contain information on the temperature
dependence of HCl/N_2 broadening. There have been two recent
studies that are the most useful to date for stratospheric work:
those of Houdeau et al. (1980) (included in the HALOE study), and
of Ballard et al. (1983), which is just now available. The
Houdeau study includes both HCl/N_2 and HCL/O_2, at 298 K and 163
K, from which one may calculate the temperature dependences of
the broadening coefficients. The estimated uncertainties of the
measurements is 5%. The Ballard et al. study is only of HCl/N_2,
but with a much more extensive temperature study. Their
uncertainties are 3-4% for the strong lines near band center.
Both studies include all the lines likely to be used in
atmospheric studies, including lines that will contribute
significantly to HALOE and PMR measurements. Over the range P_5
to R_7, the range of commonality, the average disagreement at 235
K, appropriate to the mid-stratosphere, (from the measured
numbers of Ballard et al. at 235 K and power law interpolations
of the 298 K and 163 K Houdeau et al. values) is 7%. Both sets
of numbers are substantially lower than the Toth and Darnton
(1974) values, which are currently on the AFGL listing.

Line strengths for the HCl rotational lines are analogous
to those of HF, in that they may be calculated to greater than 1%
accuracy directly from the static dipole moment.

We have found no determinations of line broadening
parameters for the rotational lines of HCl in the literature. In

this sense, the situation is worse than that of HF, since the lines are similarly saturated. The relatively advanced state of knowledge of the HCl (0,1) line broadening parameters, including temperature dependence, would be very useful if it could be transferred directly to the (0,0) case, but it is difficult to quantify the common wisdom that pressure broadening coefficients are the same for different vibrational transitions. There is an experimental study on the (0,0) and (0,1) bands of HCl broadened by Ar, by Smith and Giraud (1977), which indicates that the correspondence is good to 10% in that particular case, but nothing else to go by except theoretical studies; in searching for an analogous case, we note that the (0,0) and (0,1) HF/N_2 numbers presently available are not of sufficient accuracy to warrant a qualitative comparison.

(B) Stratospheric Measurements

The past several years, roughly the tenure of the BIC program and the ongoing analysis of results, has coincided with a shift in spectral analysis techniques for most investigators doing discrete line measurements of HCl and HF (and, of course, all of the other important stratospheric trace species). The change has been from line equivalent width measurements or, in a few cases, comparison of measured and synthetic spectra, to nonlinear least-squares fits of measured spectra to synthetic spectra calculated using quite sophisticated radiative transfer modelling of the atmosphere. However, there are apparently no atmospheric profiles yet in the literature for either species

derived by the new least-squares fitting methods. For column measurements , a full nonlinear least squares treatment may not be justified, since uncertainty due to the shape of the profile may exceed the uncertainty to which the spectra can be fit (see Mankin and Coffey, 1983). Some reanalysis of older data using the more modern techniques is already underway, for example, the reanalysis of the 1978 Bomem data by Jae Park at NASA/LaRC.

Several problems that can affect both the absorption and emission balloon-borne measurements of HF and HCl remain to be addressed by most investigators: (1) Instrumental field-of-view effects can significantly broaden the effective weighting functions used in a profile retrieval, and may need to be included in the radiative transfer calculations. (2) Flight pressures and temperatures need to be measured in a fashion consistent with prime scientific data. The pressure measurement can be accomplished straightforwardly by including a calibrated capacitance manometer as part of the scientific package, but local temperature measurement from a balloon gondola is difficult.

The history of stratospheric measurements is fairly long: 1973 to the present for HCl and 1974 to the present for HF, including measurements in both hemispheres. The thrust of the BIC campaign is to resolve differences in measurement and analysis techniques, and to separate these from real atmospheric differences. Hopefully, one result will be that a full enough understanding of atmospheric measurements is reached to make the full record of HCl/HF measurements of use in understanding trends

in atmospheric composition.

HF   The stratospheric investigations of HF are summarized in
the World Meteorological Organization report (Hudson, 1982, Table
1-22), to which the following additions should be made: Carli et
al. (1980), Girard et al. (1982), Girard et al. (1983), Mankin
and Coffey (1983), Traub and Chance (1981) and the recent
ground-based work of G. M. Stokes and D. W. Johnson at Battelle
Northwest Laboratories (personal communication, 1984).

For solar absorption measurements of the HF fundamental
band, the R_1 line has been used almost exclusively, except for
one of the seven investigating groups using only the R_0, one
using the R_0 and R_1, and one using the R_0, R_1, P_1 and P_2. Line
selection is governed by resolution and other instrumental
considerations; it appears to have been made with sufficient
regard for interferences in all cases that this should not
influence the results. In particular, the R_1 line appears to be
quite free of interference in the stratospheric spectrum. Line
strengths all relate back to the results of Lovell and Herget
(1962), although they have varying subsequent histories and vary
by small amounts (one study states a line strength without
attribution that is quite close to the other values). Most of
the studies predate the inclusion of HF in the AFGL listing.
Only one study includes an uncertainty due to the line strength
in the final errors.

Pure rotational lines of HF have been detected in the
stratosphere by Carli et al. (1980) and by Traub and Chance

(1981). The first actual profile of HF from our results is
included in this report. Both groups measuring HF rotational
lines are doing so by emission measurements, and both have
suffered in the past from the difficulty of absolute pointing,
which is being addressed by the design of suitable gyroscope- and
inclinometer-based stabilization systems.

The only current evidence of the variability of
stratospheric HF is that found in Mankin and Coffey (1983), who
see both temporal and latitudinal variations substantially above
their level of precision in the column density of HF above 12 km.

HCl   The stratospheric HCl investigations are also summarized
in the WMO report, with the following additions: Carli et al.
(1980), Chance et al. (1980), Girard et al. (1982), Girard et al.
(1983), Mankin and Coffey (1983), Traub and Chance (1981), and
Stokes and Johnson (personal communication, 1984).

The fundamental vibrational lines of HCl that have been
used most extensively for measurement of stratospheric
concentrations are the R_1 and R_2 lines of $H^{35}Cl$, although at
least six other lines have been utilized in addition. The bulk
of the information always comes from the $H^{35}Cl$ R_1 and/or R_2
lines. Lines strengths for most of the investigations come from
Toth et al. (1970), since the investigations predate the
inclusion of HCl parameters on the AFGL listing. More recent
investigations use the AFGL strengths, whose genesis is described
above. Most investigators have either used the weak line
approximation or have used the Toth et al. self-broadening

parameters for line saturation effects (excepting, of course, recent investigators using the AFGL numbers). Only one reference was found for the use of an actual N_2 broadening study of HCl line broadening, that of Rank et al. (1963).

The groups measuring rotational lines of HCl (Traub and Chance, Carli et al.) have similar difficulties to those encountered for HF. There is a larger choice of lines than for HF, but the difficulty with line saturation is as severe. The comments on absolute pointing apply equally as well to HCl. Our first profile for stratospheric HCl is also included as part of this report.

Mankin and Coffey (1983) also have measurements showing significant temporal and latitudinal variation of the HCl column density above 12 km, well outside their limits of experimental precision. Girard et al. (1982,1983) have data showing substantial variation of the HCl column density above 11.5 km with latitude, obtained over a relatively short (11 day) time period in 1980.

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